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Line strengths and line shapes of zero-phonon absorption features in solid hydrogen

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Abstract Molecular hydrogen for which pure rotational and rovibrational electric dipole transitions in the free states are symmetry-forbidden, exhibits an infrared spectrum in the condensed phase caused by multipolar induction Theoretical details that are essential for the interpretation of line intensity and line shapes of zero-phonon rovibrational transitions in solid H_2 and its isotopic variants are discussed

Keywords Line intensity and line shape, solid hydrogen, infrared spectra

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1 Introduction

Solid hydrogen as the archetypical molecular quantum crystal with its fascinating low temperature behavior, seems to present endless opportunities and challenges to experimentalists and theorists alike. The special appeal of the solid hydrogens (H_2, HD etc.) to spectroscopists stems from the fact that the gas phase property of quantized end-over-end molecular rotation persists in the solid down to 0 K and spectral linewidth in the crystalline phase are almost two orders of magnitude narrower than the Doppler limited gas phase spectral lines. A particularly gratifying feature is that many of the condensed phase properties are amenable for *ab initio* theoretical analysis. In our laboratory, for many years, we have been addressing the problem of the line shapes and intensities of infrared absorption features in solid hydrogen consisting of zero-phonon single and double rovibrational transitions. One may recall that these infrared transitions are strongly forbidden in the free molecules, but occur in the condensed phase by multipolar induction [1]. It is clear therefore that knowledge of the various multipole moments of H_2 are essential for the correct interpretation of the absorption intensities. In this context rovibrational matrix elements, most accurate till date, of the multipole moments and polarizabilities of H_2 both in free and solid phase have been computed by us [2]. Recently, we extended some of these calculations to the heavier isotopomers of the H_2 molecule. Certain aspects of the line shapes and intensities of absorption features in solid hydrogen and the latest developments in this field, particularly, the contribution from our laboratory, will be reviewed in the present paper.

One may recall that because of the symmetry requirements on the total wavefunction, including the nuclear spin, homonuclear diatomic molecules such as H_2 and D_2, exist in two quasi-metastable ortho and para modifications which in many experiments can be regarded as distinct, stable molecular forms [3]. The ortho-H_2 modification refers to molecules with total nuclear spin angular momentum quantum number $T = |\vec{I}_1 + \vec{I}_2| = 1$ and rotational angular momentum quantum number J odd (the so called "antisymmetric" levels [3]), and para-H_2 to $T = 0$ and J even (the "symmetric" levels [3]). On the other hand ortho-D_2 corresponds to $T = 0$ or $T = 2$ and J even, while para-D_2 goes with $T = 1$ and J odd. At the low temperatures at which solid samples have to be necessarily studied, only the $J = 0$ and $J = 1$ levels are appreciably occupied and the solid can be regarded as a mixture of molecules in the spherically symmetric $J = 0$ and the flattened or elongated $J = 1$ states. Since techniques have been developed which make possible experimentation on H_2 and D_2 solids with any desired ortho-para concentration ratio, these solids offer unique opportunity to study the anisotropic

interactions and molecular orientation phenomena The HD molecule is, of course, heteronuclear and hence there is no para or ortho modification of HD All the molecules in solid HD are normally in the $J = 0$ state.

2. The typical spectrum in solid hydrogen

The homonuclear molecules like H_2 and D_2 do not have a permanent dipole moment and therefore pure rotational and rovibrational electric dipole transitions in the free state are symmetry-forbidden. However, these molecules exhibit an infrared spectrum in the condensed phase which arises from the electric dipole moments induced by the multipolar interactions among the molecules [4–8] Since the spectrum results from the multipole field-induced dipole moment which is the property of a pair of molecules, not only transitions due to single molecules but also simultaneous transitions of individual molecules in a H_2 pair upon absorption of one photon - the so called double transitions, are observed Also, the induced dipole moments, among other things, depend on the order of the multipolar induction as well as on the intermolecular separation. As the intermolecular separations are constantly being modulated by the lattice vibrations, it is natural to expect the lattice modes to get coupled to the inner rovibrational excitations in the individual molecules

The infrared absorption of the solid hydrogens typically consists of two parts : relatively sharp features each of which is accompanied by broad absorption contours on the higher frequency side as shown in Figure 1 The sharp lines are interpreted to be transitions among the levels associated with

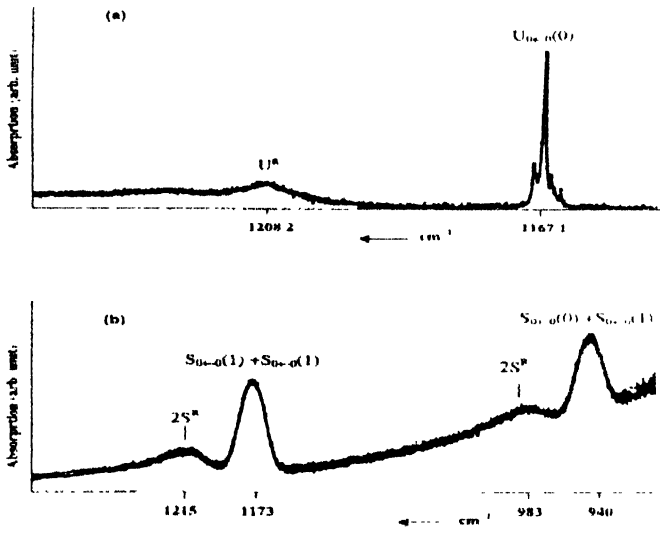

Figure 1. Typical zero-phonon single and double IR transitions and associated phonon branches in solid H_2 (a) shows the pure rotational single transition $U_{0\leftarrow 0}(0)$ in solid para-H_2. U^R is the associated phonon branch and (b) shows the pure rotational double transitions $S_{0\leftarrow 0}(0) + S_{0\leftarrow 0}(1)$ and $S_{0\leftarrow 0}(1) + S_{0\leftarrow 0}(1)$ The respective phonon branches are denoted by $2S^R$ The symbols S and U stand for transitions with $\Delta J = J' - J'' = 2$ and 4, respectively The numerals in brackets refer to J'' (= 0 for para and 1 for ortho) The subsripts describe the vibrational transition ($v' \leftarrow v''$)

the internal degrees of freedom of one molecule (single transitions) or a pair of molecules (double transitions) without any phonons being involved in the process and are termed "zero-phonon lines" The accompanying broad bands represent combination tones in which the absorption of a single photon excites an internal transition in one or a pair of molecules with the simultaneous creation of phonons in the crystal. Historically these have been called "phonon branches".

3. Theoretical preliminaries : origin of the spectrum

The basic experimental quantity that is directly relatable to line intensity is the integrated absorption coefficient α defined as :

$$(c/Nl)\int \ln(I_0/I)\,dv/v,$$

Here c is the speed of light, I_0 and I are, respectively the incident and transmitted intensities, v is the wavenumber of the line (in cm^{-1}), l is the sample length and N is the number of the absorbing molecules per cm^3 Theoretically, α is related to the matrix elements of the induced dipole moment μ as [3]

$$\alpha \quad (8\pi^3/3h)\sum_{n,n} \left| \langle m_f | \mu_{ind} | i n_i \rangle \right|^2 d_i ,$$

where $|i n_i\rangle$ and $|f n_f\rangle$ are the initial and final states, n_i and n_f being the respective degeneracy labels, and d_i ($2J'' + 1$) is the degree of the initial state degeneracy. The task of developing expression for α for any specific transition thus reduces to one of evaluating the appropriate expression for the induced dipole moment

The theoretical origin of the various zero-phonon single and double transitions in relation to the induction mechanism has been outlined by Van Kranendonk and reviewed by Silvera and Rao *et al* [4–7] In order to gain some insight into the induction mechanism, consider a pair of molecules 1 and k as shown in Figure 2 Molecule 1 is placed at the origin of a

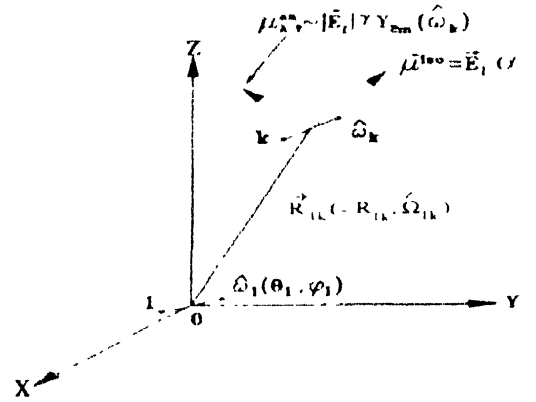

Figure 2. Isotropic and anisotropic dipole moment induction in H_2 molecule k by the ℓ-th order multipole field of H_2 molecule 1 at the origin α and γ are, respectively, the isotropic and anisotropic polarizabilities of molecule k For exact expressions for μ^{iso} and μ^{an} see [8–10]

laboratory fixed coordinate system XYZ. The center of the molecule k is located by the position vector $\boldsymbol{R}_k$. The orientation of the axes of the two molecules is given by $\hat{\omega}_1 (= \theta_1, \phi_1)$ and $\hat{\omega}_k (= \theta_k, \phi_k)$. The electric field at molecule k, due to the 2^ℓ-pole moment of molecule 1 would polarize k to produce in it an induced dipole moment $\mu_{\text{ind}}(1, k)$. This has an isotropic component μ^{iso} parallel to the field and another anisotropic component (due to the anisotropic part of the polarizability tensor) which is dependent on the orientation of k. Symbolically, one can write as

$$\mu^{\text{iso}}(\ell, 1, k) \sim \left[Q_\ell(1) . Y_{\ell m}(\hat{\omega}_1) . R_{1k}^{-(\ell+2)} \right] . \alpha(k) , \tag{3}$$

$$\mu^{\text{an}}(\ell, 1, k) \sim \left[Q_\ell(1) . Y_{\ell m}(\hat{\omega}_1) . R_{1k}^{-(\ell+2)} \right] . \gamma(k) . Y_{2m}(\hat{\omega}_k) \tag{4}$$

In the expressions above, $Q_\ell(1)$ is the 2^ℓ-pole moment of molecule 1, α and γ are, respectively, the isotropic and anisotropic parts of the polarizability of molecule k and $Y_{\ell,M}$ a spherical harmonic. Note that Q_ℓ, α and γ parametrically depend on the internuclear separation (r_1 or r_k) in the respective molecule. Explicitly, the moment Q_ℓ, is given by

$$Q_\ell(r) = \left\langle \sum e_i \rho_i^\ell P_\ell(\cos\theta_i) \right\rangle , \tag{5}$$

where the summation is over the electrons as well as the nuclei in the molecule and the expectation value is over the electronic ground state. For centro-symmetric molecules like H_2, Q_ℓ is non-zero only for even values of $\ell \geq 2$. However, there is no such restriction for heteronuclear molecules like HD *etc*. The explicit expressions for the (lab-frame) spherical components of the two parts of the multipole induced dipole moments which are needed for quantitative calculations can be found in [8–10].

From the structure of eq. (3) it is clear that μ^{iso} can cause rovibrational transition in molecule 1 obeying the selection $\Delta J \leq \ell$ with or without a pure vibrational transition in molecule k. The former results in a double transition of the type $[\Delta J \leq \ell]_{v_1 \leftarrow 0}(J_1) + Q_{v_k \leftarrow 0}(J_k)$ and in the latter case we have a single transition. The number in parenthesis is the rotational quantum number $J (= J'')$ of the molecule in its lower state. At the temperature of solid-H_2 (< 14 K), we essentially have $J = 0$ for a para molecule and $J = 1$ for an ortho molecule. The symbol Q here stands for a transition in which $\Delta J = (J' - J) = 0$. The subscript in the transition indicates the change in vibrational quantum number v, the lower state always being $= 0$ for absorption spectra. The relation for μ^{an}, namely, eq. (4) suggests the possibility of a different kind of double transition in which both molecules in the pair $(1, k)$ can change their rotational states with $\Delta J_1 \leq \ell$ and $\Delta J_k \leq 2$, but without any restriction on their vibrational transitions. The expressions (5.3) and (5.4) restrict only the rotational transitions that the individual molecule can perform in the pair. However, there is no restriction on the vibrational transitions which makes it possible to observe pure rotational as well as rovibrational transitions in the fundamental and overtone regions.

4. Scaling laws for the intensities

It is interesting to unravel from eqs. (2)–(4) the scaling laws that govern the intensities of the multipole field-induced dipole spectrum *vis-à-vis* the strengths of the multipole radiation of the corresponding order in the isolated (free) molecule. There is hardly any discussion of this aspect in the published literature. To fix our ideas, let us compare the quadrupole moment-induced dipole absorption strength $\tilde{\alpha}[E1;\ Q_2$ induced] in nearest neighbor pair in solid para-H_2 with the quadrupolar absorption strength $\alpha[E2]$ in the free H_2 molecule. From eqs. (2) and (3) we have, $\tilde{\alpha}[E1;\ Q_2$ induced] $\sim (8\pi^3/3h)\ Q_2^2\ \alpha^2/R_{1k}^8$ (α is the polarizability and Q_2 is quadrupole moment). From the standard theory of multipole radiation one can obtain : $\tilde{\alpha}[E2] \sim (8\pi^5/3h)\ \sigma^2\ Q_2^2$ ($\sigma = 1/\lambda$ is the wavenumber of the transition). Thus,

$$\frac{\tilde{\alpha}[E1;\ Q_2\text{-induced}]}{\tilde{\alpha}[E2;\ Q_2\ \text{free molecule}]} \sim \frac{\alpha^2 \lambda^2}{\pi^2\ R_{1k}^8} \sim 10^5$$

showing that the quadrupole moment induced dipole spectrum is 5 orders of magnitude stronger than the free molecule quadrupole spectrum.

Yet another interesting and more elegant scaling rule is obtained by comparing the absorption strengths of transitions due to interaction by the $2^{\ell+2}$ moment and 2^ℓ moment (with $\ell = 2, 4, 6, etc$. In centro-symmetric systems like H_2, moments with $\ell = 1, 3, 5, etc$. vanish). From eqs. (2) and (3) we may write,

$$\frac{\tilde{\alpha}[E1, Q_{\ell+2}\text{-induced}]}{\tilde{\alpha}[E1, Q_\ell\ \text{induced}]} \sim \frac{Q_{\ell+2}}{Q_\ell}\ \frac{R_{1k}^{2\ell+4}}{R_{1k}^{2\ell+8}}$$

In atomic units we may write $Q_\ell \sim e a_0^\ell$ (e-electronic charge, a_0-Bohr radius), so that the above ratio reduces to $\sim (a_0/R_{1k})^4$ where we may identify R_{1k} with the nearest neighbor distance (~ 3.8 Å for solid H_2). In contrast to this situation, if one were to observe directly the corresponding multipolar transition of successive orders in the isolated molecule, the ratio of the absorption strength would have scaled as :

$$\frac{\tilde{\alpha}[E\ell+1, Q_{\ell+1}, \text{free molecule}]}{\tilde{\alpha}[E\ell;\ \text{free molecule}]} \sim \left(\frac{a_0}{\lambda} \right)$$

(λ-typical transition wavelength). From the foregoing we deduce that in general $\tilde{\alpha}[E1;\ Q_\ell$ induced] scales as $(a_0/R_{1k})^{2\ell}$ whereas $\tilde{\alpha}[E\ell;$ free molecule] goes as $(a_0/\lambda)^{2\ell}$. In solid H_2, $R_{1k} \sim 3.8$ Å, whereas λ is a typical IR wavelength (~24000 Å for the origin of the fundamental band). The fact that in solid

H_2, up to now one has been able to observe transitions with $\Delta J = 8$ (induced by Q_8-pole) has much to do with the overwhelmingly favorable scaling laws governing the strengths of the induced spectrum. The induced spectrum thus affords a means of experimentally determining the various multipole moments of H_2.

5. Line intensities of zero-phonon transitions

In Section 3 we discussed possible transitions which can be caused by isotropic and anisotropic components of induced dipole moment. To calculate the absorption intensity of zero-phonon single transitions, the net induced moment (μ^{so}) is first obtained by summing the induced dipole moment $\mu^{so}(\ell; 1, k)$, due to a pair of molecule, over all the molecules in the crystal (of course molecule 1 is excluded). The matrix element to be used in eq. (2) is then obtained between the initial state $v'' = 0, J'' = 0$ (or 1) and the final state $v' = v, J' = \ell$ (or $\ell + 1$). In the case of double transitions one first evaluates the matrix element of μ_ℓ (pair 1, k) between the appropriate (product) initial and final states of the molecular pair (1, k) and substitutes the result in eq (2) to obtain the partial absorption coefficient $\tilde{\alpha}(1,k)$ for the pair. The net absorption coefficient is then given by the sum $\sum_k \tilde{\alpha}(1, k \neq 1)$. While the theory of absorption intensities of all kinds of single transitions and double transitions in para-H_2 pair has been discussed extensively by Balasubramanian *et al* and Ma *et al* [10–12] ten years back, the intensities of similar transitions involving ortho-para pair, described as "mixed double transitions", awaited theoretical elucidation for want of experimenta data at that time. A good number of the mixed double transitions were observed recently by Winnewisser's group in Giessen [13,14] and subsequently, theoretical formulas were developed by Mishra and Balasubramanian [1] for their intensities.

It is evident from eqs. (2)–(4) that correlation of experimental intensities to theoretical predictions calls for a knowledge of the matrix elements of Q_ℓ, $\alpha(k)$ and $\gamma(k)$ between rovibrational states of molecules 1 and k, characterizing the transition. In order to obtain the rovibrational matrix elements essentially, one computes the integral

$$\langle vJ|f(R)|v'J'\rangle = \int \chi_{vJ}(R) f(R) \chi_{v'J'}(R) dR \qquad (1)$$

where $f(R) = Q_\ell(R)$, $\alpha(R)$ or $\gamma(R)$ and $X_{vJ}(R)$ denotes the rotation–dependent vibrational wavefunctions defined in the center of mass (CM) reference frame. Rovibrational matrix elements, most accurate till date, of the multipole moments up to rank 10 of H_2 and all its isotopic variants have been computed by us [2,15–17]. It is worth mentioning that for the heteronuclear varieties HD, DT *etc.* the calculations become a non-trivial exercise due to the non-coincidence of the geometric charge center with the center of mass (CM) of the molecules. Therefore, for the heteronuclear isotopomers it is necessary to first transform the bond distance-dependent multipole moment functions to the CM coordinates. As a result, the computations had to include even as well as odd values of ℓ, unlike for their homonuclear counterparts H_2 *etc.* wherein only even ℓ can occur. More details may be obtained from [16].

An exhaustive listing of the polarizability matrix elements are given by Hunt *et al* [17]. However, it turned out that certain of the off-diagonal polarizability matrix elements involving $\Delta v \leq 1$, needed in the absorption intensity calculation, are not listed in this paper and had to be computed afresh by us [18] using the (more accurate) r-dependent polarizability functions given Rychlewski [19]. We believe these are more accurate than the earlier results [17]. We also studied the effect of intermolecular potential on the matrix elements of Q_ℓ, $\alpha(k)$ and $\gamma(k)$ when the molecule exists in the solid phase. It turned out that this effect is indeed negligible as may be seen from the comparison of the gas phase and condensed phase matrix elements of Q_ℓ between certain selected states given in Table 1. This is as expected since hydrogen forms a weak solid.

Table 1. Comparison of the gas phase and condensed phase adiabatic matrix elements of the 2^ℓ-pole moments Q_ℓ ($= Q_\ell/ea_0^\ell$) of H_2

v	J	$<0J\|Q_2\|vJ+2>^a$		$<0J\|Q_4\|vJ+4>^a$		$<0J\|Q_6\|vJ+6>^a$		$<0J\|Q_8\|vJ+8>^a$		$<0J\|Q_{10}\|vJ+10>^a$	
		Gas[b]	Cond	Gas[b]	Cond	Gas[b]	Cond	Gas[b]	Cond.	Gas[b]	Cond
0	0	0 484 732	0 485 602	0 340 92	0 342 30	0 226 3	0.227 8	0 155 3	0 156 6	0 114 3	0 115 5
0	1	0 486 855	0 487 728	0 345 55	0.346 96	0 232 1	0.233 6	0 161 3	0.162 7	0.120 3	0 121 6
1	0	0 078 242 5	0 078 330 8	0 118 78	0 119 23	0 114 9	0 115 6	0.099 15	0.099 98	0.085 02	0 085 92
1	1	0 071 963 0	0.072 039 9	0.110 73	0.111 14	0 107 9	0 108 6	0 093 83	0.094 62	0.080 99	0 081 85
2	0	-0 011 635 3	-0 011 668 7	-0 000 607	-0.000 631	0 011 91	0.011 97	0 018 87	0.019 02	0.021 49	0 021 71
2	1	-0 011 818 0	-0 011 850 7	-0 033 116	0.003 148	0 007 68	0.007 71	0 013 92	0.014 02	0 016 27	0 016 44
3	0	0.001 928 7	0 001 935 5	-0.001 707	-0.001 713	-0 002 83	-0 002 85	-0.002 04	-0 002 07	-0.001 21	-0 001 23
3	1	0 002 129 9	0 002 137 1	-0.001 196	-0 001 199	-0 002 64	-0.002 66	-0.002 40	-0 002 43	-0.002 03	-0.002 07

[a] In atomic units. [b] From [2]

6. Line shapes

The spectrum shown in Figure 1 illustrates that the single transition $U_{0\leftarrow 0}(0)$ in the ~100% para-H_2 solid is quite sharp while the double transitions are broad. This is due to solid state interactions. In the presence of intermolecular interaction, the rotational/vibrational excitation in a molecule in the crystal will no longer be expected to remain localized and there occurs the formation of roton or vibron energy bands in the solid. The hopping of the rotational excitation from molecule to molecule is driven by the dominant electric quadrupole-quadrupole anisotropic interaction. Corresponding to the $v = 0, J = 2 \leftarrow 0$ pure rotational excitation a roton band of width ~2 cm^{-1} has been observed [5]. Likewise the $v = 1, J = 0$ pure vibrational excitation in a pure para-H_2 crystal is broadened into a vibron band of width ~3 cm^{-1}, due to the isotropic part of the intermolecular interaction [5]. Each travelling wave solution of the exciton problem is characterized by a Block vector $\boldsymbol{k}$ spanning the Brillouin zone. The width associated with the higher excitations are, as a rule, several orders smaller since (weaker) higher order terms in the intermolecular potential are involved in their propagation and the widths of these excitation bands, as explained in [7], are reflected only in the double transitions. In the single transitions, the requirement of momentum conservation, including the crystal momentum $\hbar\boldsymbol{k}$, forbids accessing of all energy states in a band except those in the vicinity of $|\boldsymbol{k}| \approx 0$. In the presence of impurities, which may even be ortho-H_2 molecule, the periodicity of the lattice is vitiated and all the selection rules that are incumbent on the crystal momentum conservation become less meaningful. This will result in the broadening of even the single transitions.

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